Dielectric Relaxation and Static Dielectric Constant of Confined Aqueous Solutions

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The Debye relaxation of bulk liquid water is a collective response of the electronic dipoles of water molecules that interact through a hydrogen bonding network. Water relaxation results from structure and dynamics beyond near-neighbor interactions and hence is sensitive to any process, solute or substrate that influences the hydrogen bond network. Below 100 GHz, water relaxation is well described by a single relaxation time constant of about 8ps at 25°C, decreasing at higher temperature. Solutes can introduce either higher or lower frequency contributions depending on solvation interactions. We are using broadband dielectric spectroscopy (BDS) at 0.1–50 GHz to study the effects of spatial confinement on the structure of water and aqueous solutions.

We used a network analyzer to measure broadband dielectric response of natural and synthetic clay minerals, and diatomite, as a function of hydration state and temperature. The relaxation of water confined in natural smectites is slower than bulk and water in diatomite is faster, a surprising observation we interpret as evidence of hydrophobic porosity. Complete interpretation of BDS data from natural samples is ambiguous, however, so we performed a study of well-characterized synthetic layer silicates complemented by molecular dynamics (MD) simulation. The MD simulation provide excellent predictions of BDS data as a function of hydration state and allow different types of water to be distinguished by their characteristic relaxation timescale.

The low-frequency limit of BDS can also provide good estimate of the static dielectric constant of bulk aqueous solutions, an important measure of the ion solvation properties of any geochemical fluid. Accurate quantitation of low-frequency BDS from water pores or surface films is challenging but will provide a pathway to more accurate predictions of geochemical speciation in pores.